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Low Energy Photophysics of Phenylene-Based Strapped Copolymers

by

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13. ABSTRACT (Maximum 200 words)

We present the absorption and emission properties of the phenylene-based copolymers, poly (pyridyl vinylene-phenylene vinylene) (PPyVPV), poly (thienylene *p*-phenylene) (PTpP) and poly (dithienylene *p*-phenylene) (PDTpP), which incorporate "straps" to bridge the 2 and 5 positions of the phenyl rings. The absorption and luminescence properties of the PPyVPV polymers are morphology dependent. The absorption's maxima are at ~3.0 eV, with the films having absorption edges that tail into the IR. The photoluminescence (PL) spectra are red shifted for films compared to solutions and powders, with the presence of smaller red shifted photoluminescence for the PPyVPV polymers with straps. A low-lying absorption maximum occurs at 2.7 eV for both solution and film forms of PTpP. The (PL) spectra also are similar with features at 2.1 eV and 2.3 eV assigned to the 0-1 and 0-0 vibronic transitions, respectively. Solution and film photoluminescence excitation (PLE) profiles qualitatively follow the absorption spectra. Two low energy absorption maxima are seen for PDTpP at 2.8 eV and 3.2 eV with a single feature observed at 2.3 eV for the PL. The PLE spectra in PDTpP also follow the corresponding absorption features in both solution and film samples. Time resolved PL studies (ps to ns) show that there is smaller spectral shift for the films of polymers with straps, showing the importance of reduced aggregation. Steady state photoinduced absorption studies (ms) indicate the roles of both polarons and triplet excitons in these systems.

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Low Energy Photophysics of Phenylene-Based Strapped Copolymers

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ABSTRACT

We present the absorption and emission properties of the phenylene-based copolymers, poly(pyridyl vinylene-phenylene vinylene) (PPyVPV), poly(thienylene *p*-phenylene) (PTpP) and poly(dithienylene *p*-phenylene) (PDTpP), which incorporate "straps" to bridge the 2 and 5 positions of the phenyl rings. The absorption and luminescence properties of the PPyVPV polymers are morphology dependent. The absorption's maxima are at ~ 3.0 eV, with films having absorption edges that tail into the IR. The photoluminescence (PL) spectra are red shifted for films compared to solutions and powders, with the presence of smaller red shifted photoluminescence for the PPyVPV polymers with straps. A low lying absorption maximum occurs at 2.7 eV for both solution and film forms of PTpP. The (PL) spectra also are similar with features at 2.1 eV and 2.3 eV assigned to the 0-1 and 0-0 vibronic transitions, respectively. Solution and film photoluminescence excitation (PLE) profiles qualitatively follow the absorption spectra. Two low energy absorption maxima are seen for PDTpP at 2.8 eV and 3.2 eV with a single feature observed at 2.3 eV for the PL. The PLE spectra in PDTpP also follow the corresponding absorption features in both solution and film samples. Time resolved PL studies (ps to ns) show that there is smaller spectral shift for the films of polymers with straps, showing the importance of reduced aggregation. Steady state photoinduced absorption studies (ms) indicate the roles of both polarons and triplet excitons in these systems.

Keywords: luminescence, pyridene, PPV, poly(pyridyl vinylene-phenylene vinylene), spectral shift

1. INTRODUCTION

The advent of poly(*p*-phenylene vinylene) (PPV) as an efficient emissive layer within light emitting devices (LEDs) has opened many developments within the conjugated polymer community over the last several years.^{1,2} In particular, researchers have focused upon making longer lasting and more efficient polymer LEDs. One means of achieving such a goal is by understanding the underlying photophysical processes of the luminescent conjugated polymers.

We present an overview of the photophysical properties of the pyridine-based polymers PPy, PPyV and copolymers made up of PPyV and PPV (PPyVP(R₂V) with various sidegroups, including straps, used to keep the polymer chains well separated and soluble in differing solvents. From absorption and luminescence studies, the primary excitations in pyridine-based polymers are singlet excitons. In addition, there are conformational differences between samples of differing morphology: Films cast from either formic acid or tetrahydrofuran (THF) solution are susceptible to aggregate formation (regions where both the ground and excited state wave functions are delocalized over several chains). Time resolved PL studies show a spectral shift of the emissions for films demonstrating the effects of aggregation. Photoinduced absorption (PA) on powder, solution and film samples of PPyV further support the exciton picture, showing enhanced triplet exciton production in powders in addition to direct observance of singlet to triplet exciton conversion on the picosecond time scale. Through millisecond PA, triplet excitons and polarons are determined to be the dominant long-lived species. The volume density of triplet excitons is larger in powders than films, once again supporting enhanced triplet production in this morphology. Studies of PTpP and PDTpP with straps show that these systems have less aggregation.

2. EXPERIMENTAL PROCEDURES

The polymer samples, schematically shown in Fig. 1, were synthesized as powders.^{3,4,5,6} In this paper, we refer to three different forms of the pyridine-based polymers: powders, solutions and films. "Powder" refers to the as-precipitated solid form

obtained directly after the synthesis has occurred. These powders could then be dissolved to form solutions of various concentrations. Films could then be either drop- or spin- cast onto quartz substrates from the solutions. The optical studies of the powder forms were performed by dispersing the polymer in KBr (~0.02%-0.04% by mass) and pressing the subsequent mixture into a pellet form. Solutions were prepared by dissolving the polymer in formic acid (HCOOH), for PPyV and PPy, and spectroscopic grade THF, for the copolymers. Details of the spectroscopy facilities are discussed elsewhere.^{789,1}

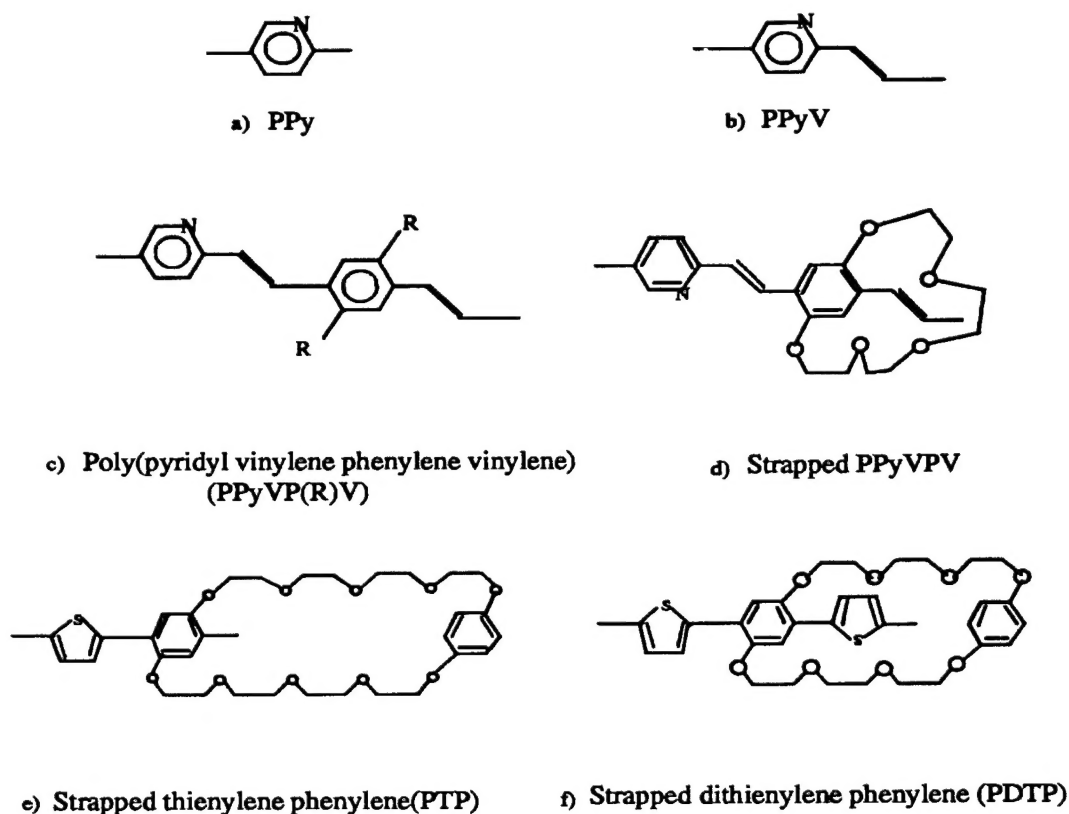


Fig 1. Schematic structure of (a) PPy, (b) PPyV, (c) Poly(pyridyl vinylene phenylene vinylene) (PPyVP(R)V), (d) strapped PPyVPV, (e) strapped thienylene phenylene (PTP), (f) strapped dithienylene phenylene (PDTP)

3. ABSORPTION AND PHOTOLUMINESCENCE

Figure 2 compares the optical absorption spectra of solution, powder and film forms of PPy and PPyV with that of each of the copolymers (Figure 1c) for energies less than 4.5 eV. Examining the solution and powder spectra for PPyV, there is little difference in the optical absorption: the absorption edges ~ 2.5 eV with maxima ~3.0 eV. Film spectra have a longer tail into the IR (absorption edge ~ 2.4 eV) and peak around 3.0 eV indicating that there is little overall change in the distribution of conjugation sites when comparing to powder and solution forms. The longer tail into the IR is a result of the formation of aggregate states within the polymer sample.⁷⁻⁹ Each of the three copolymers whose absorbance is shown in Figure 2, as well as PPy, behave similarly. Additionally, the photoluminescence excitation (PLE) spectra for films compared to powder and solution forms of each polymer are redshifted, peaking at an energy within the tail of the absorption and very near the peak in the PL.⁷ The latter forms have PLE spectra lying very near the peak in the lowest lying absorption feature with a larger apparent Stokes shift. The copolymers show little overall change in the low energy photophysics with respect to the parent polymers. The only observed differences are a redshift of the direct and photoinduced absorption and PL by ~0.2-0.4 eV and carbonyl formation which quenches the PL and PA signals of the copolymer with the alkoxy sidegroup, (PPyVP(OC₁₆H₃₃)₂V).⁷ Similar results have been reported for alkoxy derivatives of PPV.¹⁰

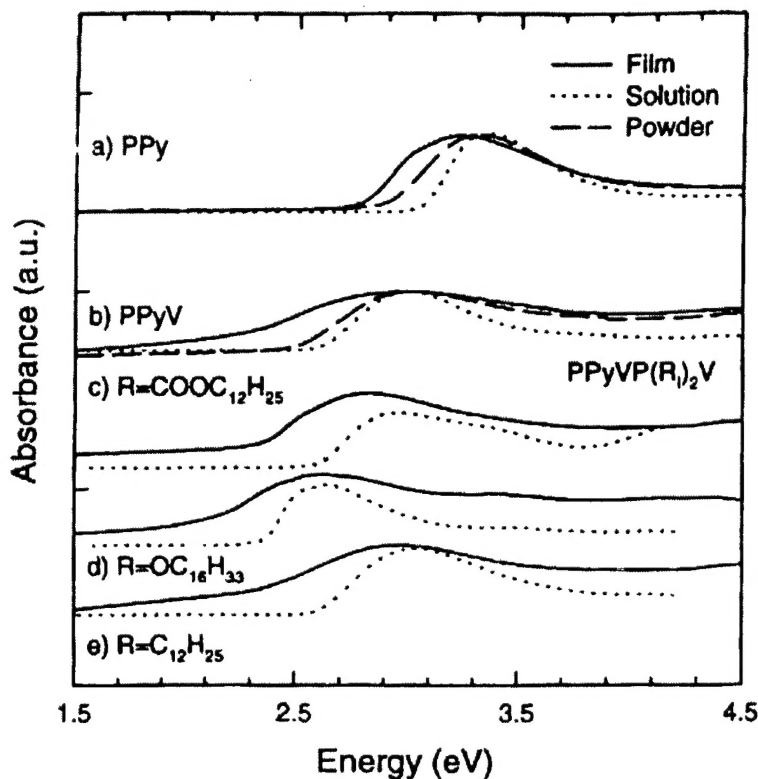


Fig. 2. Optical absorbance in film (solid), solution (dotted) and powder (dashed) forms of a) PPy, b) PPyV, c) PPyVP(COOC₁₂H₂₅)₂V d) PPyVP(OC₁₆H₃₃)₂V and e) PPyVP(C₁₂H₂₅)₂V.

The photoluminescence for dilute solution ($< 10^{-5}$ M), powder and film forms of PPyV (top), PPy (middle) and a representative copolymer (bottom) are shown in Figure 3. For each of the polymers the powder and solution PL spectra are similar; however the film spectra are redshifted by as much as 0.5 eV indicating that emission in films comes from lower energy sites. The PL efficiencies of solutions are quite high for the copolymers (~70-90%), but are lower for PPyV and PPy (~10%-20%). Additionally, the PL in solutions is very nearly independent of concentration, suggesting that excimer formation is not occurring in solution. The solution PL decays are almost single exponential (~90%) and are independent of wavelength in all the materials except PPy where there is a slight redshift with time. The radiative lifetime is found to be ~1-2 ns for the polymers studies.⁹

The large apparent Stokes shift (~0.5 eV) between absorption and emission spectra in solution and powder forms stems from exciton migration to lower energy segments followed by radiative or nonradiative decay. Site selective fluorescence studies yield an intrinsic Stokes shift of ~60 meV,⁹ a result comparable to that found by Bässler and coworkers^{11,12} for PPV indicating that exciton migration is applicable to these systems. In addition, Huang-Ryss analysis on PPyVP(OC₁₆H₃₃)₂V yields a relaxation energy ~86 meV for the pyridine-based polymers with strong coupling to the 1300 cm⁻¹ C=C stretching mode of the vinylene unit,⁹ indicating a relatively weak geometrical relaxation for the singlet exciton.

Corresponding with the increased oscillator strength in the IR absorption, in all cases the film PL is redshifted with respect to the solution PL by ~0.5 eV. Furthermore, the internal quantum efficiencies for films are quite low, ~1/3 - 1/2 of the solution values.⁹ Aggregate sites act to reduce the luminescence efficiency of films, as the radiative lifetime of aggregate excitons is longer than that of intrachain or solution-like excitons. The powder PL spectra once again strongly resembles that of solutions. These results taken in conjunction with the absorption results indicate that both the absorption and luminescence are dependent upon the morphology of the sample. The degree of aggregation in film samples being dependent upon the type of solvent used and the method of preparation.⁹

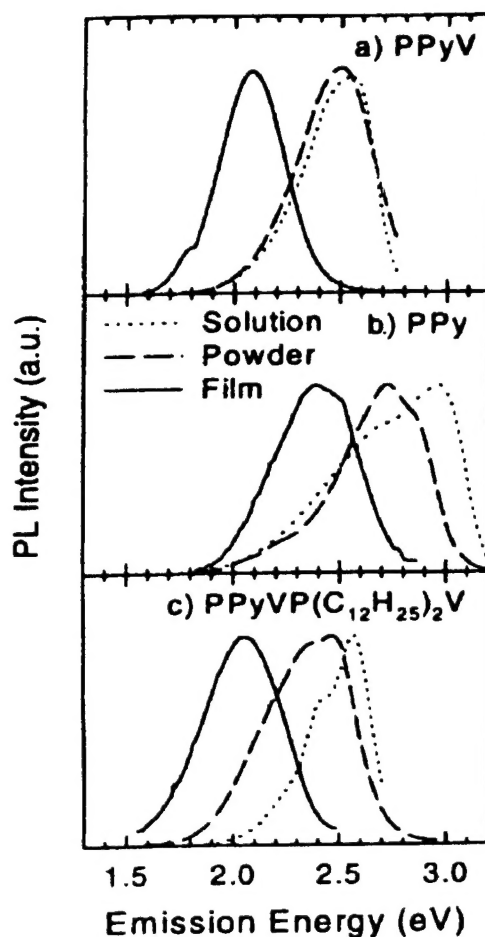


Fig. 3 Photoluminescence of solution (dotted), powder (dashed) and film (solid) forms of a) PPyV, b) PPy and c) PPyVP(C₁₂H₂₅)₂V.

The absorbance of a xylenes solution of wrapped PPyVPV, Figure 4, peaks at an energy similar to that of the unstrapped copolymers and PPyV. The strapped PPyVPV xylenes solution excitation spectrum closely follows the absorption curve, without any clear vibronic structure, similar to the behavior of PPyVPV solution in THF.¹³ The photoluminescence spectrum has an apparent Stokes shift of ~0.5 eV, again similar to the unwrapped polymer.⁷ These results can be compared to those for strapped PPyVPV film, Figure 5. Though there is only a small red shift of the absorbance and PLE upon formation of the film, there is a larger red shift and a lack of vibronic structure of the PL, similar to the behavior of PPyVPV films,⁷ suggesting that some aggregation still occurs despite the presence of the straps. However, film samples of the strapped PPyVPV do have a high energy shoulder in their PL, supporting that some regions are no longer aggregated as a result of addition of the straps.

The absorbances of films of PTpP and PDTpP show a very small red shift when compared with the corresponding absorbances for xylenes solutions, Figures 6 and 7. In all cases the absorption edge is approximately 2.4 eV. There is only a small increase in the Stokes shift of the PL in going from solution to film for each of these polymers, with the PTpP showing a slightly larger shift. For both polymers the vibronic structure observed in solution is maintained for the films. Both PTpP and PDTpP have high quantum efficiencies (QE) of ~ 80% (PTpP) and ~ 55% (PDTpP) in xylene solution. A dramatic reduction in QE occurs in cast films with QE ~ 5% for PTpP and QE < 1% for PDTpP.

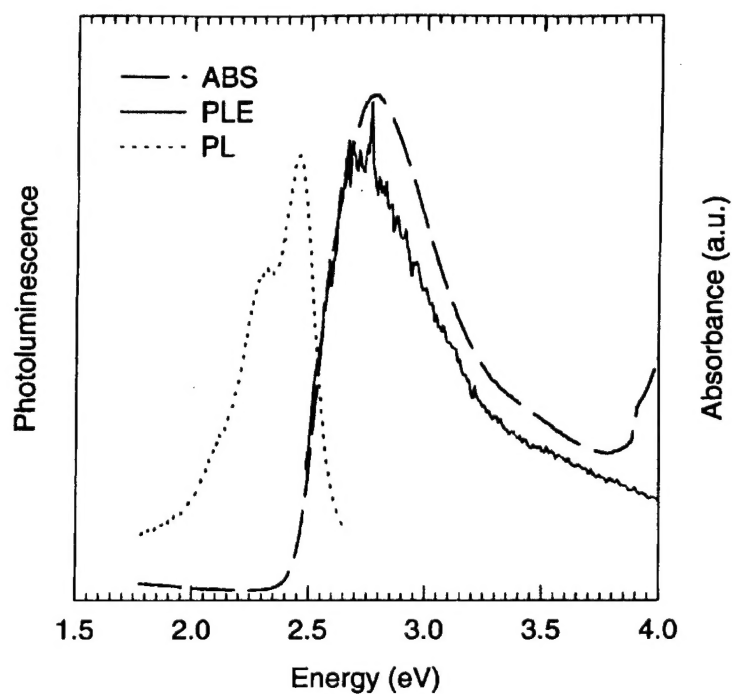


Fig. 4. Optical absorbance (solid curve), photoluminescence excitation spectrum (dashed curve) and photoluminescence spectrum (dotted curve) of strapped PPyVPV in xylenes solution. Solution concentration adjusted to a maximum absorption of $< \sim 10\%$.

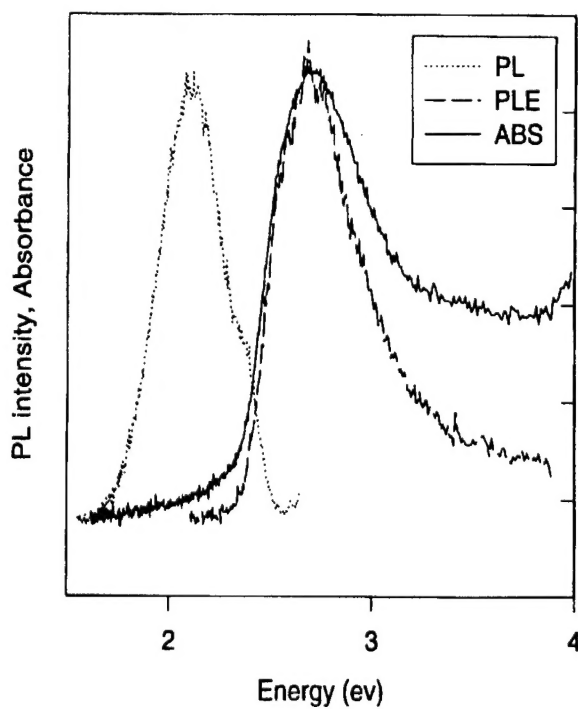


Fig. 5. Optical absorbance (solid curve), photoluminescence excitation spectrum (dashed curve) and photoluminescence spectrum (dotted curve) of strapped PPyVPV film.

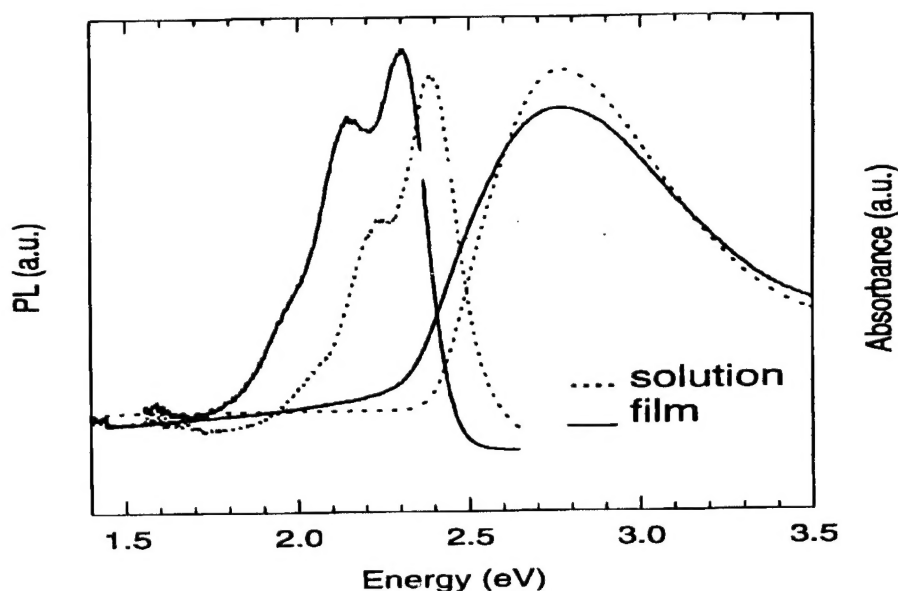


Fig. 6. Optical absorbance and photoluminescence spectrum of xylenes solution (maximum absorption $< \sim 10\%$) (dotted curves) and film (solid curves) of PTPP.

3. TIMED RESOLVED PHOTOLUMINESCENCE AND PHOTOINDUCED ABSORPTION

Earlier time resolved photoluminescence studies of PPyV in HCOOH solutions showed a nearly single exponential decay, with 90% of the decay accounted for by a ~ 400 ps component.⁹ This single exponential behavior together with a lack of Stokes shift between the PL emission and excitation spectra in solution, shows that the primary photoexcitation in solution is a Coulomb-bound singlet exciton.⁹ In contrast, the time resolved PL of the PPyV films shows a marked spectral shift with time. The results show rapid migration of the singlet excitons to the aggregate regions.¹³ Similar spectral shifts with time due to aggregation are observed for the PPyVPV copolymer (Fig. 1c) films. Though the solution of the strapped PPyVPV shows as similar single exponential decay, the films of the strapped copolymer show a substantially reduced spectral shift with time, demonstrating the effect of the strap in reducing effects of aggregation.⁷ The PTPP and PDTpP polymers also have nearly single exponential decay of their PL when in solution. The spectral dispersion of the PTPP and PDTpP films PL is even less than that of strapped PPyVPV demonstrating the smaller susceptibility of the PTPP and PDTpP polymers to aggregation.

Millisecond photoinduced absorption studies of PPyV shows the presence of a triplet-triplet transition at ~ 1.8 eV (especially in PPyV powders) and polaron excitations 0.9 eV and possibly 1.8 eV. Similar studies of PTPP reveals the triplet-triplet transition at ~ 1.4 eV, at lower energies than the corresponding transition in pyridine based polymers. Also, photoinduced absorptions at 0.6 and 2.1 eV are associated with possible polaron transitions, lower in energy than the corresponding transitions for the PPyV system and its copolymers. The relatively large triplet signal for the PTPP polymer may arise from enhanced intersystem crossing (from singlet to triplet exciton manifold) that occurs with the large chain twists expected in the presence of the straps.

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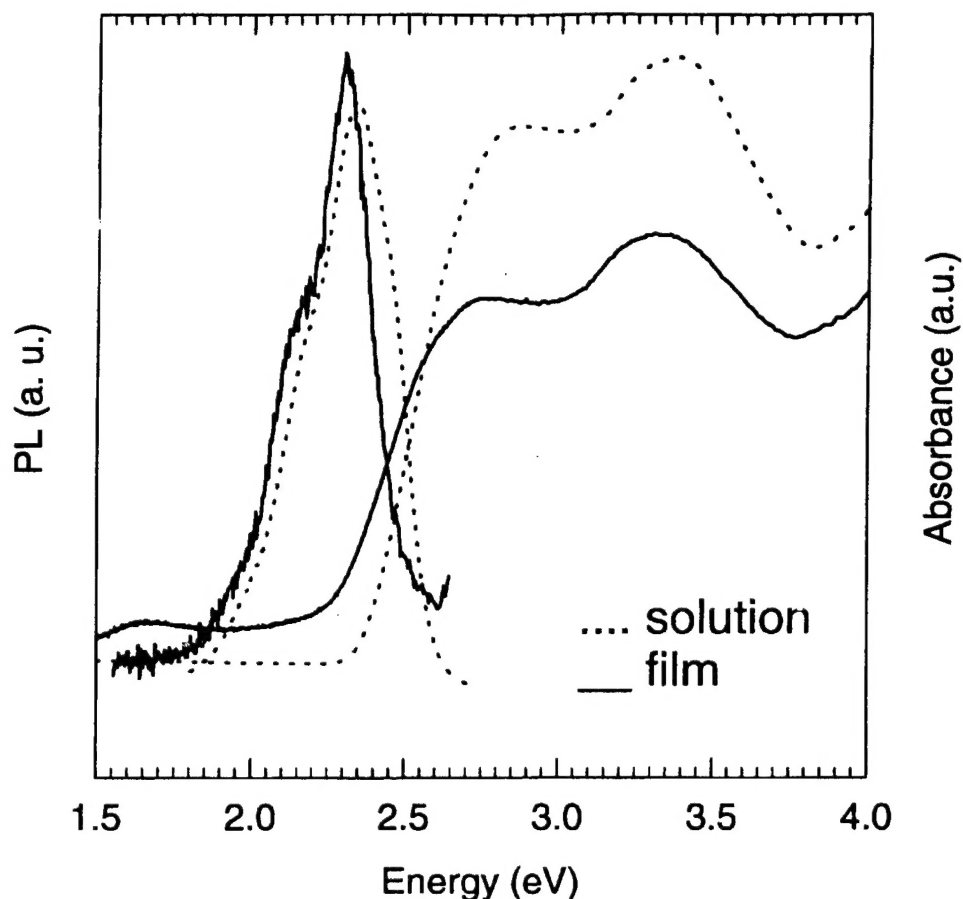


Fig. 7. Optical absorbance and photoluminescence spectrum of xylenes solution (maximum absorption $< \sim 10\%$) (dotted curves) and film (solid curves) of PDTpP.

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